

CLAIMS

1. A method for composition control of copper indium gallium diselenide (CIGS) solar cells fabricated by a co-evaporation deposition process in a process chamber, the deposition conditions being such that a deposited Cu-excessive overall composition is transformed into to a Cu-deficient overall composition **characterized by**
 - a. performing said co-evaporation process in the process chamber of an in-line, continuous substrate flow production system,
 - b. detecting where the transition from copper rich to copper deficient composition occurs by using a physical parameter related to the same transition, said instant referred to as a reference transition point.
 - c. detecting a shift of the transition point using the physical parameter, and
 - d. adjusting the evaporant fluxes in order to bring the transition point back to the reference transition point.
2. A method in accordance with claim 1, **characterized by** performing said detection at at least one location as seen in a direction over the width of a substrate.
3. A method in accordance with claim 2, wherein a substrate provided with a molybdenum back contact layer moves through the CIGS process chamber **characterized in** that the physical parameter is monitored at two points, one at each side of the position the CIGS layer has in the process chamber at the reference transition point, in order to detect the position at which the transformation occurs, said position referred to as a reference position.
4. A method in accordance with claim 3, wherein heating elements are arranged at each side of the position at which the transition occurs **characterized by** holding the power delivered to the substrate constant and measuring a temperature difference at two adjoining heating elements at the reference position.
5. A method in accordance with claim 3 **characterized by** holding the temperature of the substrate and deposited CIGS film constant by supplying individually

controlled power to the heating elements and measuring a difference in the power delivered at two adjoining heating elements at the reference position.

6. A method in accordance with claim 3, wherein a several pairs of sensors distributed over the width of the process chamber, are used for detection at said two points, **characterized by** assigning each sensor pair a respective set of evaporation sources and adjusting the evaporation flows in each evaporation set individually in order to bring the respective transition points back to their reference transition positions.
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7. A method in accordance with any of claims 3-6, wherein a pair of sensors is used for detection at said two points, **characterized by** adjusting the copper flux in each set.
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8. A method in accordance with claim 3, **characterized in** that the physical parameter is related to the emissivity of the CIGS layer.
9. A method in accordance with claim 3, **characterized in** that the physical parameter is heat capacitivity or, as is known per se, resistivity.
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10. A method in accordance with claim 3, **characterized in** that the physical parameter relates to intensity of light reflected by or transmitted through the deposited CIGS film.
11. A method in accordance with claim 3, **characterized in** that the physical parameter relates to intensity of specular light in relation to intensity of reflected light.
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12. A method in accordance with any of claims 1-11, **characterized by** the further step of detecting the deposited amount of constituents of the CIGS film.
13. A method in accordance with any of claims 1-11, **characterized by** providing sets of evaporation sources (11, 12, 13) in rows over the width of a substrate (21) and controlling the evaporant fluxes in the respective rows.
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14. A method in accordance with claim 13, **characterized by** the further step of detecting the deposited amount of constituents of the CIGS film.

15. An in-line continuous substrate flow production apparatus for fabrication of copper indium gallium diselenide (CIGS) solar cells comprising a CIGS process chamber (7) in which substrates (2) provided with a molybdenum back contact layer (3) continuously move through a deposition zone (DZ) in the CIGS process chamber, the process chamber comprising a plurality of separated heating elements (10) **characterized by** at least one sensor (18, 19; 30, 31) arranged in deposition zone and connected to a controller, the sensor being adapted to measure a physical parameter related to a transformation of the deposited CIGS film from a Cu-excessive composition to a Cu-deficient composition, said transformation taking place at a reference transition point (27) in the process chamber as the substrate moves through the process chamber, the sensor being arranged to detect a shift of the actual transition point on the moving substrate from the reference transition point by measuring the physical parameter at the deposited CIGS film at the reference transition point, the controller (17) being adapted to receive as input the sensor output signal and to deliver as output a corrective signal that adjusts the evaporant fluxes so that the actual transition point is brought back to the reference transition point.
16. An in-line production apparatus in accordance with claim 15, **characterized in that** two sensors together forming a sensor pair (18, 19) are arranged at each side of the transition point, that each sensor in the pair is connected to a respective input of the controller, said sensor pair being arranged in a row with the evaporation sources.
17. An in-line production apparatus in accordance with claim 15 or 16, **characterized by** a device (17) for detecting the deposited amount of constituents of the CIGS film.
18. An in-line production apparatus in accordance with claim 15, wherein a sensor pair is associated with an individual set of evaporation sources (11-13), **characterized in that** two sensor pairs (18, 19) are arranged at different locations as seen in a direction over the width of the process chamber, that each sensor pair and its associated set of evaporation sources are arranged in a respective row, and that each sensor pair and set of evaporation sources of a

row is connected to a respective controller (17) so as to adjust the evaporation flows in each evaporation set.

19. An in-line production apparatus in accordance with claim 18, wherein there are two rows each one comprising a set of evaporation sources (11-13),
5 **characterized by** providing the two rows of evaporation sources at each side of and outside the path along which substrates flow through the deposition chamber (7).
20. An in-line production apparatus in accordance with claim 18 or 19,
10 **characterized by** a device (17) for detecting the deposited amount of constituents of the CIGS film.
21. An in-line production apparatus in accordance with claim 17, **characterized in that** the device for detecting the deposited amount of constituents of the CIGS film is an XRF (X-ray fluorescence) device, an EDX (energy dispersion X-ray spectroscopy) device or a profilometer.
- 15 22. An in-line production apparatus in accordance with claim 18, **characterized in that** additional sensor pairs and associated evaporation sources (11-13) are arranged in a row at a location between said two rows.
23. An in-line production apparatus in accordance with claim 22, **characterized in that** one or more additional sensors (30, 31) are connected to an input of the
20 respective controllers (17), the additional sensors being arranged to measure the physical parameter upstream and/or downstream the reference transition point.
24. An in-line production apparatus in accordance with claim 15, **characterized in that** the controller (17) is adapted to change the relative amount of Cu versus
25 In+Ga.
25. An in-line production apparatus in accordance with claim 15, **characterized by** an x-ray fluorescence composition measurement device (20) adapted to measure the total deposited amounts of each element (Cu, Ga, In, Se) and thereby the thickness and composition of the deposited CIGS layer.

26. An in-line production apparatus in accordance with claim 25, **characterized in that the controller (17) is connected to the x-ray fluorescence composition measurement device (20) and is adapted to adjust the total amount of deposited Cu and/or the total amount of deposited Ga+In in order to keep the thickness of the deposited CIGS layer constant.**
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27. A method for composition control of copper indium gallium diselenide (CIGS) solar cells fabricated by a co-evaporation deposition process in a process chamber (7) comprising evaporation sources (11-13, 26) with Cu, In, Ga and Se, said method comprising the step of measuring the individual amounts of elements in the deposited layer **characterized by** providing sets of evaporation sources (11, 12, 13) in rows over the width of a substrate (21), measuring the individual amounts of elements in the deposited layer in each row, and controlling the evaporant fluxes in the respective rows in order to provide a CIGS film of uniform composition of elements.
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28. A method in accordance with claim 27, **characterized by** measuring the total thickness of the deposited CIGS film at each of the rows and adjusting the flux from at least one of the individual evaporation sources (11-13) in order to provide a CIGS film of uniform thickness.
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29. A method in accordance with claim 27, wherein there are two rows each one comprising a set of evaporation sources (11-13), **characterized by** providing the two rows of evaporation sources at each side of and outside the path along which substrates flow through the deposition chamber (7).
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30. A method in accordance with any of claims 27-29, **characterized by** taking the measurements inside the process chamber.
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31. A method in accordance with any of claims 27-29, **characterized by** taking the measurements outside the process chamber.
32. An in-line continuous substrate flow production apparatus for fabrication of copper indium gallium diselenide (CIGS) solar cells comprising a CIGS process chamber (7) in which substrates (21) provided with a molybdenum back contact layer (3) continuously move through a deposition zone (DZ) in the CIGS process chamber, the process chamber comprising a plurality of separated substrate
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heaters (10), evaporation sources (11-13, 26) with Cu, In, Ga and Se, and source heaters (14, 15, 16) **characterized by** providing sets of evaporation sources (11, 12, 13) in rows over the width of a substrate (21), at least one composition detection device (20) for detecting the respective amounts of deposited elements in the CIGS at each of the rows, and a controller (17) connected to said at least one composition detection device and adapted to adjust the evaporant fluxes in the respective rows in response to a detected variation in deposited amount of the corresponding element in order to provide a CIGS layer of uniform composition of elements.

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10 33. An in-line continuous substrate flow production apparatus in accordance with claim 32, **characterized by** said at least one composition detection device (20) being adapted to measure the deposited amount of constituents of the deposited CIGS film at each of the rows, and said controller (17) being adapted to adjust the evaporant fluxes in the respective rows in order to provide a CIGS film of uniform thickness.

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20 34. An in-line continuous substrate flow production apparatus in accordance with claim 32 or 33, wherein there are two rows of vapour sources arranged over the width of the process chamber as seen in the transport direction of the substrates, **characterized by** arranging the two rows of evaporation sources at each side of and outside the path along which substrates flow through the deposition chamber (7).

35. An in-line continuous substrate flow production apparatus in accordance with claim 32 or 33, **characterized by** providing said at least one composition detection device (20) within the process chamber.

25 36. An in-line continuous substrate flow production apparatus in accordance with claim 32 or 33, **characterized by** providing said at least one composition detection device (20) outside the process chamber.

37. An in-line continuous substrate flow production apparatus in accordance with claim 32 or 33, **characterized by** arranging the evaporant vapor sources (11-13) at a level below the substrates (21).

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38. An in-line continuous substrate flow production apparatus in accordance with claim 32 or 33, **characterized in that** said at least one composition detection device (20) is a device that measures the composition of the CIGS layer directly.
39. An in-line continuous substrate flow production apparatus in accordance with 5 claim 32 or 33, **characterized in that** said at least one composition detection device (20) is an (X-ray fluorescence) device and/or an EDX (energy dispersion X-ray spectroscopy) device is adapted to measure the total deposited amounts of each element and thereby also the thickness of the CIGS layer.
40. An in-line continuous substrate flow production apparatus in accordance with 10 claim 32 or 33, **characterized in that** the controller (17) is adapted to receive as input signal a signal representative of the total deposited amounts of each element and in response to said latter signal adjust the fluxes from the evaporant sources (11, 12, 13) in order to provide a uniform thickness of the CIGS film.
41. An in-line continuous substrate flow production apparatus in accordance with 15 claim 32 or 33, **characterized in that** said at least one composition detection device is a device that measures the composition of the CIGS layer indirectly.
42. An in-line continuous substrate flow production apparatus in accordance with 20 claim 32 or 33, **characterized in that** said at least one composition detection device is a resistance measuring device.
43. An in-line continuous substrate flow production apparatus in accordance with 25 claim 32 or 33, **characterized by** a separate thickness measuring device connected to the controller for measuring the thickness of the deposited CIGS layer, the controller being adapted to adjust the fluxes from the evaporant sources (11, 12, 13) to in response to a detected thickness variation in order to provide a CIGS layer of uniform thickness.
44. An in-line continuous substrate flow production apparatus in accordance with claim 43, **characterized in that** the thickness measuring device is a profilometer.

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45. An in-line continuous substrate flow production apparatus in accordance with claim 32 or 33, wherein there are evaporant sources with Cu, Ga and In **characterized in that** the evaporant sources are arranged in the following order as seen in the transport direction of a substrate: Ga, Cu, In.
- 5 46. An in-line continuous substrate flow production apparatus in accordance with claim 45, **characterized by** a further evaporation source with Ga arranged downstream the In evaporation source.
- 10 47. An in-line continuous substrate flow production apparatus in accordance with claim 32 or 33, wherein there are evaporant sources with Cu, Ga and In **characterized in that** the evaporation sources are arranged in the following order as seen in the transport direction of a substrate: In, Cu, Ga.
48. An in-line continuous substrate flow production apparatus in accordance with claim 47, **characterized by** a further evaporation source with In arranged downstream the Ga evaporation source.

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